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A STUDY OF THE QUALITY OF PLATINUM WARE

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I. INTRODUCTION

At the request of Dr. W. F. Hillebrand, Chairman of the Committee on Quality of Platinum Utensils of the American Chemical Society, experiments on the loss in weight associated with continued and repeated heating of platinum crucibles of varying degrees of purity have been undertaken, in continuation of similar experiments carried out under the immediate supervision of members of the above-mentioned committee.

From some of these earlier experiments, and from the work of other observers on the evaporation of metals of the platinum group, it appears to have been hoped that it would be possible to classify platinum ware as to purity in terms of its evaporation at a definite temperature, say 1200° C. This seemed plausible, in view of the fact that the usually predominant impurity, iridium, is very much more volatile than platinum. Even if this method,

however, does give an indication of the platinum purity, it is at best a somewhat tedious and delicate operation to carry out.

In view of the results obtained from this investigation, in which is shown the relatively great effect of extremely minute quantities of admixtures of iridium and iron on the properties of platinum, especially vapor pressure, it may be questioned if some of the results obtained by other experimenters, who have studied quantitatively the volatilization of the platinum metals, are not subject, in certain cases, to some slight modification, as in general there has been no check on the purity of the materials used by them.

Systematic observations on the disintegration of the platinum metals under the action of high temperatures have been made by a number of experimenters, as shown in the appended bibliography, but a quantitative study of the effects of impurities on the disintegration of platinum, we believe, had not been made before the experiments herein described.

II. THERMOELECTRIC DETERMINATION OF PLATINUM PURITY

The preliminary experiments showed the desirability of having an accurate and rapid method for determining platinum purity, and one that could be applied to crucibles without defacing them and which would serve also as a ready means of classification of the several grades of platinum.

The most exact method for such determination appears to be by measurement of the temperature coefficient of electrical resistance, which quantity has a mean value of about 0.00391 per degree centigrade for the interval 0° to 100° C for the purest obtainable platinum, and decreases with the addition of anything to the platinum. This measurement can be made conveniently and exactly only with wires, and is therefore of little interest for the determination of the purity of platinum ware such as crucibles.

The thermoelectromotive force of platinum against many of its alloys has also been determined with considerable exactness.¹

¹ See, in particular, W. Geibel, *Zs. Anorg. Chem.*, 69 (1910), p. 38; 70 (1911), p. 240; Burgess and LeChâtelier, "The measurement of high temperatures," 3d ed., 1912, p. 171.

This property may evidently be made use of, therefore, in devising a method for the determination of platinum purity and one that possesses, furthermore, the advantages of accuracy, speed, convenience, and preservation intact of the objects tested. It is only necessary to have at hand a chart or table of the emf's of pure

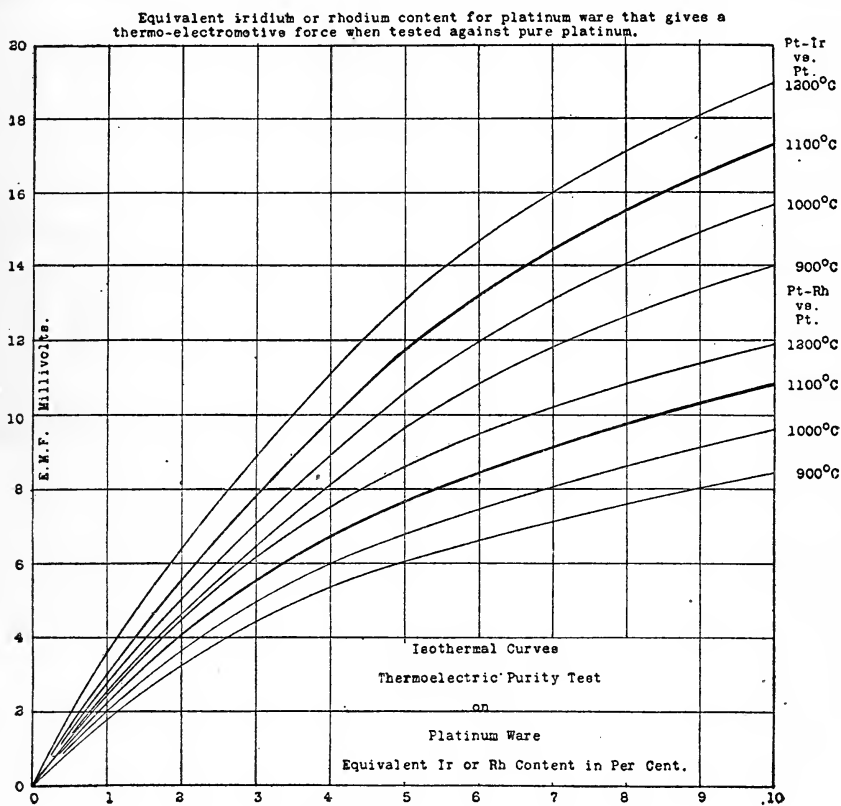


FIG. 1.—Isothermal Curves for Ir or Rh Content of Pt

platinum against its alloys with rhodium and iridium and a convenient experimental arrangement for measuring these emf's.

Such a chart is shown in Fig. 1, in which the emf in millivolts of the alloy against pure platinum is plotted in terms of the equivalent iridium or rhodium content. There are thus shown the isothermal curves for each alloy up to 10 per cent of the alloying element and for each 100° C from 900° to 1200°.

The experimental realization of the emf method as developed for use with crucibles is shown in Fig. 2. To the rim of the crucible *C* are arc-soldered, at *e* and *f*, two pure platinum wires of small diameter (0.1 or 0.2 mm); these wires are connected to an ordinary pyrometer-galvanometer or millivoltmeter, *G*; the junction *e* is heated by a small oxy-gas or other blast flame from *d*, and the junction *f* is kept cool by an air blast, *c*; a sheet of asbestos, *A*, cut as shown, serves to prevent radiation from the heated portion of the crucible reaching the cold junction *f*.

Temperatures are measured by means of a 90Pt-10Rh, Pt thermocouple using the cold junction as above, and a Pt-Rh wire arc-soldered to the crucible near *c*, most conveniently adjacent to (0.5 to 1 mm distant) but not touching the Pt wire at *e*.

The wires are attached at *e* and *f* by the well-known arc-soldering method, which consists in making the crucible one terminal of an electric circuit of about 40 volts and a sharpened graphite pencil the other, with a rheostat in series. The operation of soldering consists in drawing a minute arc between pencil and crucible and at the same instant touching the wire to the crucible at this point. The end of the wire is thus fused to the crucible. With a little practice this operation may be made so that there is hardly any noticeable effect on the appearance of the crucible after the wire is removed.

Quite satisfactory results may also be obtained by simply touching the Pt wires to the crucible at *e* and *f*, or by clamping

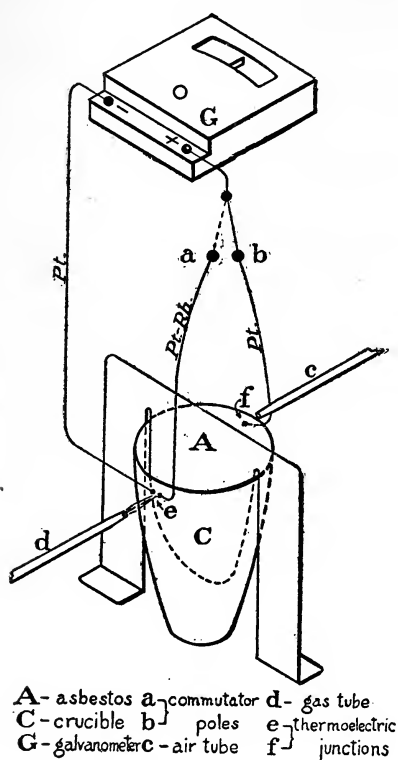


FIG. 2.—Thermoelectric purity test

with platinum clips, without any soldering. This last has been the method usually employed in these tests. With the apparatus once set up, a test may then be made in a few seconds, and the crucible remains, of course, absolutely intact. The homogeneity of the crucible may also be determined by this method.

By means of a commutator at a b measurements may be made alternately of the temperature at e and of the emf developed across the crucible when e is at this temperature. The commutator may also be designed so as to reverse e and f if it is desired to make f the hot junction. Suitable variations from the above arrangement may evidently be made for different types of ware, such as covers, gauze, needles, etc.

It is, of course, essential that the two platinum testing wires be made of strictly pure platinum. For this purpose use is made of Heraeus normal thermoelement wire drawn down. This platinum has shown itself to be a standard, uniform product, the purity of which is easily controlled by the electric resistance method above mentioned.

As an example of the uniformity which may be expected by the thermoelectric examination by the most convenient method, in which the testing wires are held by platinum clips against the crucible or other object, may be cited the observations of Table I. Observer No. 1 was experienced in the operation, observer No. 3 had had little, and No. 2 no experience in this manipulation. A portion of the irregularities noted are due to inhomogeneity of the material. This method has been found useful by ourselves and others for the ready classification of platinum utensils of various kinds and especially for the determination, in the case of purchases of platinum ware, whether or not such articles conform to specifications as to platinum purity. This thermoelectric test, which in no way mars the crucible or other article examined, is now a routine test made by the Bureau of Standards, and many samples of platinum have been so tested the past year.

TABLE 1

Electromotive Force Measurements (Millivolts at 1100° C.) on Platinum Ware by Three Observers

Description of ware	Observer	Maximum	Minimum	Probable
Crucible APW-C.....	1	7.00	6.95	7.00
	2	6.23	5.90	
	3	7.00	6.50	
Crucible 9.....	1	2.80	2.60	2.90
	2	2.18	1.92	
	3	3.00	2.40	
Crucible 11.....	1	1.88	1.38	1.94
	2	1.40	1.23	
	3	2.00	1.60	
Crucible cover 11.....	1	1.88	1.85	1.87
	2	1.86	1.52	
	3	2.20	1.50	
Crucible cover 9 ^a	1	2.05	1.06	1.03 to 2.05
	2	1.21	1.03	
	3	2.00	1.70	

^a Found to be inhomogeneous.

In Table 2 is shown the quality of platinum utensils of various sorts and from many sources expressed in terms of equivalent iridium content as measured thermoelectrically at this Bureau. Of the 164 pieces examined, which are typical of such material as found on the market, it is seen that nearly 75 per cent have impurities equivalent to over 0.5 per cent of iridium or in quantity to cause considerable losses on heating, which would be troublesome in exact analytical work; and of the crucibles 65 per cent have over 0.5 per cent equivalent iridium content. Dishes and miscellaneous ware, in which stiffness is usually required and which are often not subjected to heating and weighing, are heavily charged with impurities, usually iridium, the miscellaneous ware showing, for example, nearly half of the samples with over 4 per cent iridium. The 22 pieces of miscellaneous ware consisted of wire, boat, gauze, spatula, bottle, stopper, tubes, specially shaped ware, and scrap.

TABLE 2

Classification of Platinum Ware submitted to Bureau of Standards for Thermoelectric Purity Test

Class of ware investigated	Number pieces of each class	Per cent in each class in terms of equivalent iridium content in per cent				
		0.0 to 0.5	0.5 to 1.0	1.0 to 2.0	2.0 to 4.0	4.0 to 25
Crucibles.....	84	36	17	34	13	0
Crucible cover.....	47	26	23	38	13	0
Dishes.....	11	9	36	19	36	0
Miscellaneous.....	22	0	18	9	27	45
Total number.....	164	26	20	31	17	6

In Table 3 is shown the results of a thermoelectric test of the first 23 crucibles examined by this method.

It will be noted that all impurities are, for convenience, expressed in terms of iridium content. Of particular interest is the comparison of columns 2 and 6, the former giving the stated iridium content (and often accompanied by the statement that there are no other impurities) and the latter giving the iridium content as determined thermoelectrically by experiment and use of Fig. 1. In several instances, notably for the crucible of normal thermoelement platinum (*a*) of Heraeus and for Baker's crucible (*i*) of 2.37 per cent iridium, the stated and found iridium contents agree exactly. On the other hand, there is a wide divergence from the supposed and actual iridium content for several of the crucibles; for example, *j* of the American Platinum Works, supposed to contain not over 0.50 to 1.5 per cent iridium, actually contains an iridium equivalent of 2.50 per cent; and even in the cases of refined, specially refined, and best crucible ware the equivalent iridium content is not inconsiderable.

In comparing the stated contents (column 2 of the table), it should be borne in mind that some of these crucibles, excepting, perhaps, those marked refined or specially refined, may contain iridium which is put or left in the material purposely, usually for the purpose of stiffening, or, in the case of commercial ware, because such Pt always carried Ir. The method here described, however, provides a delicate means of determining whether or not

TABLE 3
Summary of Thermoelectric Tests of 23 Platinum Crucibles

Source or maker	Stated Ir content	Previ- ously heated	Temp. of test	EMF Pt vs crucible	Equi- valent Ir con- tent	EMF from Pt- Ir curve (see fig. 1)	EMF excess due to Ir or im- purities	Refer- ence letter	Remarks	Date of pur- chase
Heraeus.....	Per cent	Hours	°C	Mv	Per ct	Mv	Mv			
	0.0	17	1100	0.10	0.05	0.00	0.10	a	Normal thermoelement Pt.....	1911
	.7	Heated	1050	2.00	.70	2.00	.00	o	Normal Tiegel platin.....	1911
American Platinum Works.....	.7	0	1050	2.60	.90	2.00	.60	pdo.....	1911
	<.2	24	1050	.63	.19	.10	.53	d	"Tiegel platin" Heraeus.....	1911
	<.2	16	1050	1.00	.35	.10	.90	qdo.....	1911
	.5-1.5	11	1075	6.60	2.55	1.50-4.10	2.50-5.10	j	Commercial.....	1911
	.5-1.5	4	1085	6.40	2.50	1.50	4.90	rdo.....	1911
Baker & Co.....	?	.5	1100	3.50	1.19	3.50	s	Loaned by purchaser.....	1913
	?	10	1050	6.75	2.72	6.75	k	Commercial.....	1908
	?	20	1050	6.95	2.78	6.95	cdo.....	1908
	2.37	0	1030	6.00	2.37	6.00	.00	i	Special analyzed make.....	1912
	.702	12	1050	1.90	.66	2.05	—, .15	fdo.....	1912
Johnson Matthey & Co.....	Refined	0	1040	.33	.1033	t	Specially refined.....	1911
	?	a 3	1100	3.00	1.01	3.00	h	Used three years in laboratory.....	1909
	?	0	1100	1.71	.55	1.71	Average of seven commercial crucibles.....	1914
	?	67	1050	.48	.1548	b	Best crucible ware.....	1911
J. Bishop.....	?	0	1070	.68	.2368	udo.....	1911
	?	20	1050	.63	.2263	cdo.....	1913
	?	b 9	1100	2.10	.68	2.10	v	Loaned by purchaser. Used contin- uously 9 months.....	1913
	?	.5	1100	2.20	.72	2.20	wdo.....	1913
	Refined	31	1050	.60	.2160	x	Specially refined.....	1911

Quenessen, De Belmont, Legendre et Cie.	a Years.						b Months.						1911
	?	?	?	10	1050	2.79	.98	2.79	g	
	?	?	?	0	1060	2.80	.98	2.80	y	
	?	?	?	4	1030	1.60	.56	1.60	z	

the desired limitation of impurity, expressed in terms of iridium content and as measured thermoelectrically, has been met by the manufacturer. By the experimental arrangement above described, the amount of impurity may be determined to 0.01 per cent, and this accuracy might be improved upon slightly if necessary.

The method does not distinguish the various possible impurities from each other, but is nevertheless a certain check on the platinum purity. Thus, all the metals found associated with platinum, such as palladium, iridium, rhodium, etc., when alloyed with platinum (up to 90 per cent only of palladium) give, at high temperatures, an emf of the same sign against pure platinum. Therefore, there is no ambiguity in balancing one impurity against another. Although the above-described thermoelectric method will not alone distinguish between small amounts of rhodium and iridium, it may nevertheless be combined oftentimes for this purpose with other methods of examination which do not injure the crucible.

One of the most undesirable impurities often found in commercial platinum ware is iron; this is readily detected by ignition and subsequent washing with hot HCl and applying the usual tests for Fe. Iron, if present in relatively considerable quantity, will also discolor the crucible on ignition. The presence of iron is discussed at length in the following paragraphs.

III. QUALITY OF PLATINUM CRUCIBLES

In addition to data on the purity of platinum ware now in use, more exact information was desired by the committee concerning the losses on heating. The experiments here outlined, it is believed, furnish information concerning losses sustained by platinum crucibles of several grades of purity when subjected to continued heating. By suitable acid treatment after heating it has been possible to give an estimate of the relative amount of iron present, and the crucibles have also been examined microscopically and, through the kindness of Dr. Burrows, magnetically.

As will be shown, a combination of these several methods, or some of them, usually gives sufficient data for the ready classification of various grades of platinum ware.

1. METHOD OF DETERMINING LOSSES ON HEATING

For an exact determination of the loss in weight of a crucible on heating, ignition over the blast lamp is not satisfactory. A preliminary series of experiments, using electric resistance furnaces with platinum and other metals as heating coils, carried out by members of the chemical staff of this Bureau, showed that one could not expect to obtain consistently reliable results in a furnace containing metal. A considerable number of measurements of losses on heating at several temperatures were so taken, but no very definite conclusions can be drawn from these preliminary observations which were obtained before the thermoelectric method of classification was put into practice.

The method finally adopted for determining heat losses in crucibles is based on the use of a metal-free, electrically heated furnace, somewhat similar to one which had been in use for other purposes at the Geophysical Laboratory, accompanied by exact weighings of the crucible before and after each heating of two hours' duration at 1200°C , together with a weighing to determine the iron loss after washing in acid.

The essentials of the furnace are shown in Fig. 3. The heating spiral *H* is of graphite set into brass, water-cooled terminals. The crucible *C* is supported on a Marquardt porcelain stand *S*, as shown, and inclosed within a tube *T* of the same material. Temperatures were measured by a platinum, platinum-rhodium thermocouple inclosed in Marquardt. At 1200°C the furnace, which was operated on alternating current, took about 3.5 kw.

For a region of about three crucible heights at the center of the furnace there was maintained a region of practically uniform temperature, 1200°C , and this inner portion of the furnace never became blackened. A slight current of air was maintained about the crucible, as shown, but great care was taken, by means of a sand and paraffin seal at *P*, to prevent vapors passing from the heating spiral into the inner chamber. The crucible was not placed in the furnace until this had reached 1000°C ; a temperature of 1200°C was then attained in about 10 minutes and held constant for exactly two hours and cut off, the crucible being removed 10 minutes later, or at about 900°C .

Crucible weighings were made on an inclosed precision balance, at first to 0.001 mg and later to 0.01 mg, as this latter was found

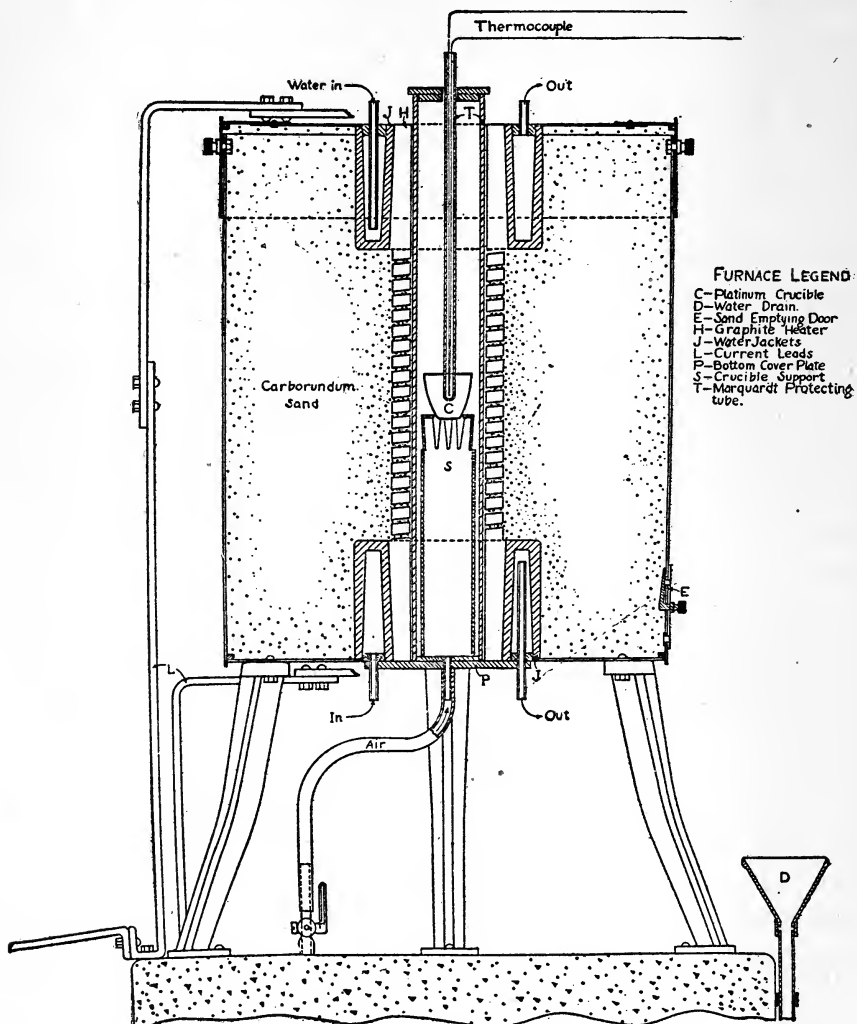


FIG. 3.—Furnace for determining losses in weight of Pt

sufficient. All weights are reduced to a common basis of loss per 100 cm² of total crucible surface.

(a) ACID TREATMENT.—Iron and other soluble materials were removed and determined by weighing after each heating. For

several of the crucibles examined the characteristic reddish coating due to iron oxide appeared after each heating. The acid treatment consisted in boiling the crucible for five minutes in 25 per cent hydrochloric acid, contained in a large covered porcelain crucible. The iron was determined by precipitation with ammonia upon ashless filter paper, ignited in platinum for one minute at about 1200°C , and weighed as ferric oxide.

2. EXPERIMENTAL RESULTS

The 14 crucibles described in Table 4 were carried through a series of identical operations, consisting of a determination of their equivalent iridium or rhodium content by the thermoelectric method (see lines I and I' of Table 5); the determination of loss of weight after each of three heatings of two hours each at 1200°C (see lines II, III, and IV), each followed by determination of loss by acid treatment (lines II', III', and IV'), and of iron content (lines IX, X, and XI). As seen from Table 6, these 14 crucibles range in equivalent iridium content from 0.05 (a) to 2.65 (l) per cent; crucibles *m* and *n* were supposed to be 90 platinum 10 rhodium, but as measured thermoelectrically contain 7.30 and 7.95 per cent rhodium, respectively, the former having been used considerably and the latter an unused crucible; some of the others are of unknown composition and the non-platinum content of each is expressed both in terms of iridium and rhodium (see lines 2 and 3 of Table 6). In Table 7 the heating and acid losses are given for four crucibles which underwent additional heatings.

(a) MICROSCOPIC OBSERVATIONS.—The microscopic observations were helpful in finally classifying the crucibles in terms of their main impurity, iridium or rhodium (see last line of Table 6), as it was found that the crystalline structures characteristic of these alloying metals, in general, imparted their appearance to the heated but otherwise unetched crucible even when present in small percentages.

The several photomicrographs shown in Figs. (a) to (n) are all of heat-etched crucibles, with a magnification of 100 diameters. They are typical of the four classes of platinum ware here dealt

with, namely, pure platinum, platinum containing rhodium, iridium, and considerable iron. The letters of the figures correspond to the lettering of the crucibles in Table 4.

Fig. (a) presents a typical appearance of the purest platinum ware obtainable. Figs. (b), (m), and (n) give the appearance of Pt-Rh ware with Rh equivalents of 0.19, 7.30, 7.95, respectively. This snarled, irregular appearance was also noted in the case of crucible *h*. It will be noticed in Fig. 4 that these crucibles gave very low volatilization on heat treatment; in fact, less than the pure platinum. It is seen (Table 4) that crucibles *m* and *n* were originally special Rh ware and that *m* had been used pretty severely in the chemical laboratory while *n* was practically new when these microphotographs were taken. Figs. (f) and (i) are typical of Pt-Ir with Ir equivalent of 0.55 and 2.30 per cent, respectively. This regular, mottled appearance of finer grain (f) contrasts with the irregular snarled appearance of the Rh ware, as noted above. Though this characteristic mottled effect was not obtained on the surface of the crucible *i* on heat and ordinary acid treatments, the small, rounded, crystalline structure with heavy boundaries is itself characteristic of Pt-Ir (see Holborn und Henning in bibliography). Figs. (e) and (l) with Ir equivalents of 0.21 and 2.65 per cent and an appreciable iron content (see 1, Table 6) constitute a fourth quality of platinum ware, viz, Pt-Ir-Fe. The size of the crystal as governed by the Ir content and also the heavy boundaries are brought out nicely here as in other photomicrographs of these last two classes. The spots and hazy appearance here are thought to be due to the presence of iron, which is in the form of iron oxide and shows itself generally after heat treatment by a dark or reddish tinge which it gives to the surface of ware so treated. All crucibles having the appearance just noted gave appreciable iron on acid treatment between heatings.

The photomicrographic analysis is not always sufficient in itself for classifying platinum ware as to quality, although it will, in general, corroborate the results of the emf, heating, and acid tests, and used with the emf test alone will usually be of sufficient certainty to decide between the predominance of iridium or rhodium impurity.



FIG. (a).—Equivalent Ir. = 0.1%. Highest purity Pt. ware obtainable



FIG. (b).—Equivalent Rh. = 0.2%. Practically new ware



FIG. (m).—Equivalent Rh. = 7.30%. After 50 severe ignitions

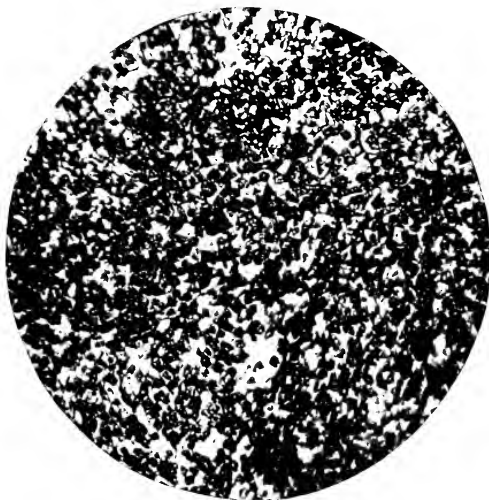


FIG. (n).—Equivalent Rh. = 7.95%. Practically new ware



FIG. (f).—Equivalent Ir. = 0.6%



FIG. (i).—Equivalent Ir. = 2.3%



FIG. (c).—Equivalent Ir. = 0.2%. Highly contaminated with iron



FIG. (l).—Equivalent Ir. = 2.7%. Highly contaminated with iron

TABLE 4
Descriptions of Platinum Crucibles (a to n)

Source or maker	Crucible reference letter	Date of purchase	Weight grams	Volume cm ³	Average thickness cm	Mean emf MV	Magnetic suscep- tibility	Previously heated hours	Factor for reduction to 100 cm ² surface
Heraeus, normal thermoelement Pt.	a	1911	17.2	26.6	0.0208	0.09	1	17	1.30
American Platinum Works, Heraeus Tiegel platin.	d	1911	16.2	21.3	.0168	.70	14	24	1.12
American Platinum Works, commercial ware.	f	1911	16.9	21.7	.0285	6.40	125	11	1.81
Baker & Co., special analyzed make.	f	1912	19.9	32.5	.0187	1.88	12	1.01
Baker & Co.	h	1909	10.8	16.4	.0183	2.98	11	(c)	1.83
Baker & Co., special analyzed make.	i	1912	20.1	30.6	.0194	6.18	0	1.04
Baker & Co., commercial ware.	k	1912	20.1	30.6	.0194	6.18	0	1.04
Do.	l	1908	23.9	33.7	.0305	6.50	10	1.27
Baker & Co., special Rh ware.	l	1908	39.6	55.5	.0342	6.90	6	20	.93
Do.	m	1913	19.9	24.0	.0235	9.30	(b)	1.27
Johnson Matthey Co., best crucible ware.	n	1913	19.9	24.0	.0235	9.70	0	1.27
Do.	b	1911	26.2	33.3	.0229	.50	26	67	.94
J. Bishop, specially refined ware.	c	1913	19.3	33.0	.0167	.64	20	.93
Quenessen, De Belmont, Legendre et Cie.	e	1911	15.9	25.5	.0190	.70	8	31	1.28
Do.	g	1911	16.3	23.7	.0193	2.80	10	1.28

b 50 ignitions (bisulphate and cleanings).

a 3 years laboratory use.

TABLE 5

Losses in Weight due to Heating and to Action of Acid on Platinum Crucibles (Milligrams per 100 cm²)

[Emf measurements: Millivolts at 1100° C. Crucible v. Pure Pt (I, I'). Heat treatment loss: Milligrams per 100 cm² for 2 hours, heating at 1200° C (II, III, IV). Acid treatment loss: Milligrams per 100 cm² for 5 minutes, boiling in 25 per cent HCl (II', III', IV'). Recovered Fe₂O₃: Milligrams per 100 cm² per treatment with NH₄OH and ignition on ashless paper (IX, X, XI, XII)]

Crucible reference letter.....	a	b	c	d	e	f	g	h	i	j	k	l	m	n
I Emf at beginning.....	0.10	0.50	0.65	0.70	0.70	1.90	2.80	3.00	6.40	6.70	7.00	7.30	9.30	9.70
I' Emf at end.....	.07	.50	.62	.70	.70	1.85	2.80	2.95	5.95	6.10	6.00	6.50	9.30	9.70
Emf mean I and I'09	.50	.64	.70	.70	1.88	2.80	2.98	6.18	6.40	6.50	6.90	9.30	9.70
II First heat, 2 hours at 1200° C.....	2.18	1.98	2.16	1.27	2.46	2.00	1.08	1.38	7.47	1.94	6.24	2.16	1.74	.61
II' First acid, 25 per cent HCl.....	.05	.24	.06	.19	.83	.16	1.76	3.82	.81	9.50	1.14	5.33	.46	.02
II+IV'	2.23	2.22	2.22	1.46	3.29	2.16	2.84	5.20	8.28	11.44	7.38	7.49	2.20	.63
III Second heat, 2 hours at 1200° C.....	.84	.96	1.93	1.36	.26	2.20	2.18	.43	4.42	4.93	5.45	2.32	1.08	1.44
III' Second acid, 25 per cent HCl.....	.30	.35	.18	.17	.56	.09	.99	1.24	.16	1.84	.39	2.47	.13	.13
III+III'	1.14	1.31	2.11	1.53	.82	2.29	3.17	1.67	4.58	6.77	5.84	4.79	1.21	1.57
IV Third heat, 2 hours at 1200° C.....	1.85	2.04	1.61	1.65	2.02	2.16	2.36	.75	4.38	3.23	2.94	5.08	1.00	1.21
IV' Third acid, 25 per cent HCl.....	.06	.15	.11	.09	.26	.07	.40	.34	.08	.66	1.01	2.79	.10	.04
IV+IV'	1.91	2.19	1.72	1.74	2.28	2.23	2.76	1.09	4.46	3.89	3.95	7.87	1.10	1.25
V ΣII, III, IV, heat loss.....	4.87	4.98	5.70	4.28	4.74	6.36	5.62	2.56	16.17	10.10	14.63	9.56	3.82	3.26
VI ΣII', III', IV', acid loss.....	.41	.74	.35	.45	1.65	.32	3.15	5.40	1.05	12.00	2.54	10.59	.69	.19
VII ΣV, VI, total loss.....	5.28	5.72	6.05	4.73	6.39	6.68	8.77	7.96	17.22	22.10	17.17	20.15	4.51	3.45
VIII Total change emf.....	.03	.00	.03	.00	.00	.05	.00	.05	.45	.60	1.00	.80	.00	.00
IX Iron as Fe ₂ O ₃ after II'.....	.147	.125099	.544	.005	1.080	.794	.052	2.520090
X Iron as Fe ₂ O ₃ after III'.....	.216	.202	— .022	.357	.113	.272	.714	.026	.603168

XI	Iron as Fe ₂ O ₃ after IV'	.103	.102123	.628	.270	.072	.454	.057	.295004
XII	Total iron as Fe ₂ O ₃	.466	.429200	1.529	.388	1.424	1.962	.135	3.418262
XIII	Total iron compared to T. L. in per cent...	8.82	7.50	5.16	23.95	5.81	16.25	24.65	.78	15.46	7.59
XIV	Total iron compared to acid L. in per cent.	100.00	58.00	53.30	92.60	100.00	45.40	36.35	12.87	28.45	100.00
XV	Total acid compared to T. L. in per cent...	7.76	12.93	9.50	25.80	4.78	35.95	67.80	6.10	54.30	5.51

TABLE 6

Classification of Ware by EMF, Volatilization, Chemical, Magnetic, and Photographic Data

Crucible Reference letter...	a	b	c	d	e	f	g	h	i	j	k	l	m	n
Mean emf millivolts.....	0.09	0.50	0.64	0.70	0.70	1.88	2.80	2.98	6.18	6.40	6.50	6.90	9.30	9.70
Equivalent Ir content, per cent.....	.05	.10	.20	.21	.21	.55	.90	1.00	2.30	2.40	2.42	2.65	3.75	3.95
Equivalent Rh content, per cent.....	.05	.19	.29	.30	.30	.85	1.29	1.40	3.53	3.70	3.75	4.15	7.30	7.95
Equivalent Fe (magnetic), per cent.....	.0001	.00220012	.0007001001100050
Weight of Fe remaining, magnetic test.....	.018	.576194	.112106	1.859198
Makers' chemical statement, per cent.....
Relative Fe by VI, Table 5..	1	1.8	.9	<.2 Ir70 Ir	2.37 Ir	5-1.5 Ir	10.0 Rh	10.0 Rh
Relative Fe by susceptibility. 1	1	26.0	1.1	4.0	.8	7.7	8.5	2.6	29.0	6.3	26.0	1.7	.5
With reference to fig. 4.....	Pt	Rh or Pt	Pt-Ir	Pt-Ir or Rh	Pt-Ir	Pt-Ir	Pt-Ir-Fe	Pt-Rh	Pt-Ir	Pt-Ir-Fe	Pt-Ir-Fe	Pt-Ir-Fe	Pt-Rh	Pt-Rh
With reference to photomicrographs.....	Pt	Pt-Rh	Pt-Ir	Pt-Ir-Fe	Pt-Ir-Fe	Pt-Ir	Pt-Ir-Fe	?-Fe	Pt-Ir	Pt-Ir-Fe	Pt-Ir	Pt-Ir-Fe	Pt-Rh	Pt-Rh

TABLE 7

Heat and Acid Losses on Four Crucibles, in Milligrams per 100 cm², After Successive Two-Hour Heatings at 1200° C

Treatment	Crucible (n)			Crucible (l)			Crucible (k)			Crucible (c)		
	Heat	Acid	Total	Heat	Acid	Total	Heat	Acid	Total	Heat	Acid	Total
First	0.98	0.00	0.98	4.30	0.77	5.07	6.24	1.14	7.38	2.16	0.06	2.22
Second	2.30	.18	2.48	2.32	2.47	4.79	5.45	.39	5.84	1.93	.18	2.11
Third61	.02	.63	5.08	2.19	7.27	2.94	1.01	3.95	1.61	.11	1.72
Fourth	1.44	.13	1.57	7.40	2.60	10.00	3.78	.60	4.38	2.34	.09	2.43
Fifth	1.21	.04	1.25	4.04	2.37	6.41
Sixth81	.06	.87
Total	7.35	.43	7.78	23.14	10.40	33.54	18.41	3.14	21.55	8.04	.44	8.48
Average values	1.23	.07	1.30	4.63	2.08	6.71	4.60	.79	5.39	2.01	.11	2.12

As an additional method for detecting rhodium, it may be mentioned that on fresh platinum ware containing considerable rhodium a characteristic bluish color appears after heating to a dull red. This test may fail, however, with ware that has been used considerably.

(b) PRESENCE OF IRON.—The presence of iron in several crucibles was also determined after the last heating and washing by measurement of the magnetic susceptibility, by a solenoid and balance method in a field of 60 gauss, and an estimate made of the relative amounts of iron present, assuming it to be free iron (see Table 6). The crucibles would hardly be arranged even approximately in the same order by chemical analysis following heating and by the magnetic measurements (see Table 6). It is also of interest to note that iron-free platinum appears to have a susceptibility of zero, and that the susceptibility of "platinum" ranges from 1 to 125. A value of about 20, in the same units, has usually been found for the susceptibility of pure platinum, due undoubtedly to the presence of iron. The total amount of iron in a crucible can not be determined readily from the magnetic measurements, as is seen by comparison of the magnetic and chemical data of Table 6; and the iron, which is supposedly in solution in the platinum, on heating diffuses to the surface as fast as removed by oxidation, thus tending to establish an

equilibrium between the iron oxide, oxygen, and the iron-platinum solution at the temperature of the experiment. The iron was found nonuniformly distributed in some of the crucibles. The iron washed out in three acid treatments is seen to be greater than the total iron content calculated as iron from the magnetic data, showing that the Fe-Pt alloy containing only a few hundredths per cent iron is paramagnetic and also, from the data, that the susceptibility is not proportional to the iron content. The discoloration sometimes noticed on first heating a new crucible, but not subsequently, may be due to iron from the finishing tools and polishing material.

(c) OTHER CONCLUSIONS FROM TABLES.—Considering further the inferences to be drawn from the results recorded in Tables 5, 6, and 7, it is seen that, taking the emf as a criterion of purity, there is a purification of all crucibles containing over 0.5 per cent iridium after heating. The platinum-rhodium crucibles (*m* and *n*) do not change composition on heating (see line VIII, Table 5); that is, the iridium passes out of the crucible and the rhodium does not appreciably.

The losses on heating and after acid treatment are seen to be fairly uniform for each crucible. For some of the less pure crucibles the loss in washing is greater than the heating loss, notably for crucibles *h*, *j*, and *l*. The total heating losses per 100 cm² range from 4.28 to 16.17 mg for six hours at 1200°, and the total acid losses (due mainly to iron) from 0.32 to 12 mg, for the crucibles containing iridium. For the platinum-rhodium crucibles, *m* and *n*, containing 7 to 8 per cent rhodium, the total losses on heating and washing together are one-fourth less than for the heating loss for purest platinum, crucible *a*. In general, there is no relation between the acid loss and loss on heating of crucibles containing both iridium and iron, showing the independence of the determination of loss of soluble and insoluble materials by these methods, although relatively large amounts of iron appear to lower somewhat the losses on heating that would otherwise be observed (see crucibles *h*, *j*, *l*). The acid losses are seen to vary from all iron to only 13 per cent iron. The remaining loss on acid treatment could be due to soluble alkaline materials, as observed first by

Dr. Hillebrand and Dr. Weber (see bibliography). However, in a series of nine crucibles tested by us, no alkalinity of the surface of the crucibles was apparent after heating. Drs. Hillebrand and Weber state: "It has been noted in varying degrees of intensity and is not always apparent."

3. PREDICTION OF LOSS IN WEIGHT DUE TO HEATING

The question arises, Can the probable loss on heating of a given crucible of unknown composition be predicted from these data? Although a definite answer can not be given, nevertheless the observations point to a reasonable probability of affirmative reply.

Consider Fig. 4, in which the heating losses are plotted against emf at 1100°C against pure platinum for each of the 14 crucibles. The purest crucibles, *a*, *b*, *c*, *d*, and *e*, all lie close together at 5 mg loss and less than 1 millivolt. The platinum-rhodium crucibles *m* and *n* lie on a line, inclined to the left of 5 mg, and which would reach to the heat loss for pure rhodium as a limit. The platinum-iridium crucibles *f* and *i*, containing negligible iron, lie on a line inclined to the right of 5 mg. The platinum-iridium crucibles, containing considerable iron, *l*, *j*, and *k*, lie between the iridium and rhodium lines, and the crucible *h*, containing considerable iron, lies to the left of the rhodium line; *h* may contain rhodium, as is also indicated by its photomicrograph.

It would follow, therefore, that one would expect a crucible, nearly free from iron (which fact is readily tested by heating over the blast lamp), and with a measured emf of, say, 8 millivolts against pure platinum, to lose 4 mg per 100 cm^2 of surface in six hours at 1200°C if made of a rhodium alloy of platinum, and would expect it to lose about 20 mg if of an iridium alloy. The distinction between these iridium and rhodium alloys may usually be made microscopically, as already shown. When iron is present, these heat losses will be reduced somewhat and may be halved, since the effective disintegration area is reduced by the layer of iron oxide. Fig. 4 may therefore be used, at least approximately, as a basis for estimating losses on heating of platinum crucibles for the usual products found on the market and Fig 4 is probably reliable for practically iron-free crucibles containing up to 40 per cent rhodium or to perhaps 10 per cent iridium.

In view of the fact that a satisfactory determination of the loss on heating for any type of crucible can be made only by elaborate experimentation, it is evidently of interest to be able to substitute for this the simple thermoelectric and microscopic tests.

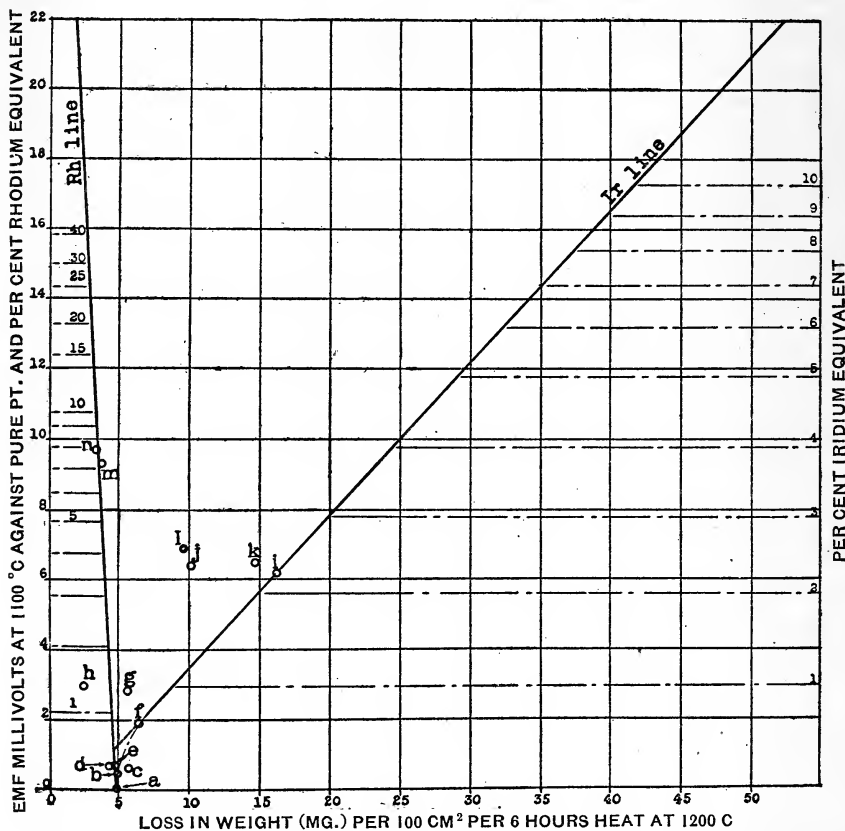


FIG. 4.—Prediction of losses in weight on heating Pt crucibles containing Ir or Rh

4. SUGGESTIONS AS TO SPECIFICATIONS

What is desired in a crucible for exact analytical work is a material which will strictly maintain its weight on heating and on treating with strong acid after heating; which will not exude any oxidizable or soluble matter on heating; which will not crack or develop other mechanical defects; and which is stiff enough to

handle conveniently with tongs. Some of these requirements appear to be simultaneously difficult of realization in the present state of our science and of the art of working platinum and its alloys.

Iridium which adds stiffness to platinum renders the crucible subject to proportionably greater losses of weight on heating. The presence of iron appears to lower materially the heat losses, but is very objectionable on account of the formation of a soluble oxide coating. The purest platinum is usually not stiff enough, although two or three of the apparently purest crucibles here examined were unaccountably stiff, perhaps because of the presence of a small amount of osmium or silica. Rhodium both stiffens the crucible and lowers the heat and acid losses and is much to be preferred to iridium as an alloying element, and crucibles containing small amounts of rhodium, say from 3 to 5 per cent, are to be preferred to crucibles of pure platinum. As the rhodium content is increased the crucible may develop cracks in service.

A requirement which might reasonably be met, at not too great expense for highest grade crucibles, would be platinum containing 3 to 5 per cent rhodium, practically free from iron and iridium, and containing no other detectable impurities. For most purposes these requirements could be checked by assuring one's self that the emf at 1100°C against pure platinum was less than 8 and greater than 5 millivolts, that the characteristic crystal structure was that of rhodium and not iridium, and that no iron hydroxide precipitate was obtained after ignition for two hours over strong blast and applying the acid treatment as above described. If pure platinum were preferred, the emf at 1100°C should be less than 1 millivolt. If other stiffening ingredients than rhodium be allowed, the 1-millivolt emf requirement should be maintained.

IV. NATURE OF DISINTEGRATION

It has been assumed or generally held until recently by investigators of the disintegration of the platinum metals on heating that the loss of weight observed is a true volatilization, but J. H. T. Roberts offers evidence to show that there is an oxidation of platinum, iridium, etc., at high temperatures, followed by a

subsequent reduction, so that the deposit carried to the cooler regions is metallic not because of volatilization but on account of an endothermic reaction between the platinum metal and oxygen forming at high temperatures an oxide which is unstable at lower temperatures.

In favor of this view appear to be the facts that these metals are less volatile at low pressures than at high, and that the presence of oxygen is essential. Against this is to be set the fact that metals, in general, have a vapor pressure which increases with temperature, and the region of stability of these oxides does not appear to have been determined.

The experiments here recorded do not give crucial evidence in favor of either of these views. The disintegration in air is shown to have a constant value for any given type of material—platinum with small additions of iridium or rhodium—and this disintegration is found to be approximately proportional to the amount of the alloying element present in platinum. Iron, when also present, as we have seen, has a special rôle of its own in retarding the disintegration.

It is possible, as Berthelot pointed out, that there might be a quantitative as well as a qualitative difference in these disintegration phenomena at high temperatures, dependent upon whether the metal is heated from outside or whether it is heated electrically from within. The experiments of Langmuir on electrically heated metal, however, indicate in high vacua an evaporation only one-twentieth of that here observed for pure platinum thermally heated at 1200° C.

The phenomena at high vacua are not, however, comparable with those at atmospheric pressure. It appears probable, therefore that there is a slight evaporation characteristic of the metal accompanied, in the presence of oxygen or air, by reaction between oxygen and platinum. Langmuir considers that "the oxygen in addition to combining with the vapor from the platinum, also attacks the platinum at a rate that increases with the pressure."

That the iridium alloys of platinum disintegrate more rapidly than platinum or its alloys with rhodium, may be due either to the greater vapor pressure of the former or to a more ready reaction with oxygen, or a combination of these two causes.

V. SUMMARY AND CONCLUSIONS

There has been devised a simple, thermoelectric method suitable for the determination of the purity of platinum ware. This method does not mar the article tested and gives data for the classification of platinum in terms of its equivalent iridium (or rhodium) content.

There were examined by the thermoelectric method 164 pieces of platinum ware, of which 26 per cent contained less than 0.5 per cent iridium and 67 per cent less than 2 per cent of iridium. Of 84 crucibles, 36 per cent contained less than 0.5 per cent iridium and 87 per cent less than 2 per cent iridium.

A method has been developed for determination of the exact loss on heating of platinum crucibles by means of a suitable electric furnace containing no heated metal parts.

Fourteen crucibles of various makes and grades were examined for loss in weight on heating and after acid treatment following each heating. Their magnetic susceptibilities were also determined. The susceptibility of pure platinum is zero and the range of susceptibility for seven crucibles is 1 to 125.

The loss of weight due to heating per 100 cm² of practically iron-free crucible surface at 1200° C, ranged from 0.71 mg to 2.69 mg per hour, the lesser losses being for crucibles containing rhodium and the greater losses being associated with iridium.

Iron appears to lessen somewhat the loss of weight on heating, but its presence is objectionable on account of the soluble oxide formed on the crucible surface. The chemical analysis and magnetic measurements place the crucibles in only approximately the same order as to iron content; the magnetic susceptibility is not, however, proportional to the iron content.

It appears to be possible, from a thermoelectric and microscopic examination of a crucible, to predict its probable loss of weight on heating within limits close enough for analytical purposes.

Suggestions are offered concerning the specifications of highest grade platinum crucibles, including the substitution of rhodium to 5 per cent for iridium, and the practical elimination of iron.

Whether crucibles have been long in use or not, after the first two or three heatings and acid washings, appears to make little or no difference in their behavior as to losses on heating and washing.

The nature of the process of disintegration of platinum and its alloys is briefly discussed.

We wish to express our obligation to Dr. W. F. Hillebrand, who has furnished many valuable suggestions which have aided the progress of this investigation.

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"On the volatilization and recrystallization of the platinum metals," by Prof. L. Holborn and Dr. F. Henning, *Sitzber, Berlin Akad. Wiss.*, p. 936; 1902.

Experiments were conducted on Ir, Rh, Pt, Pd, and Au at temperatures near their melting points; also on Pt-Rh, Pt-Ir, and Ir-Ru.

A volatilization figure was obtained for each, but data are not reduced to one basis for comparison; however, the Ir and its alloys were found more volatile than Rh and its alloys. The Pt and also Rh crystals are larger than those of Ir or Pd. Concerning the alloys, the greater the percent of Ir the smaller the crystal, and prolonged heating increases the size of the boundaries between these. The Rh alloys with Pt give a smaller and more irregular crystallization than Ir alloys. Heat etching brings out the crystallization, though etching with aqua regia is more effective.

"The volatilization of metals of the platinum group," by Sir William Crookes, *Proc. Roy. Soc. Lon.*, 86-A, p. 461; 1911-12.

Data presented in this paper show relation between volatilization of metals of platinum group. Crucibles and strips were heated in an Heraeus furnace for two-hour increments at 1300° C, 1000° to 1400° C, and 900° C in an atmosphere of still air.

The volatilization order was found to be as follows: Ru, Ir, Pd, Pt, and Rh, the last being the least volatile.

"The disintegration of metals at high temperatures" (condensation nuclei from hot wires), by J. H. T. Roberts, *Phil. Mag.*, 25, p. 270; 1913.

Condensation nuclei could be more readily produced in O than in air, and could not be produced in pure N. Some conclusions are as follows: (1) The rate of loss of Pt is zero in N, H, or a vacuum; (2) at low pressures of O the nuclei are very small; (3) the nuclei begin to be formed, i. e., disintegration begins, at a fairly definite temperature (500° C); (4) the nuclei for a given temperature and pressure are persistent and do not alter in size; they are unaffected by light or by an electric field.

The rate of loss of weight of the platinum wire being roughly proportional to the oxygen pressure points to the formation of an endothermic oxide. "This theory of the formation of an endothermic, volatile, and dissociable oxide explains all the observed facts in a perfectly simple manner and without any other assumptions."

"Disintegration of the platinum metals in different gases," by L. Holborn and L. W. Austin, *Phil. Mag.*, 7, p. 388; 1904.

Observations on each metal were made in the following order: (1) In air at atmospheric pressure; (2) in vacuum; (3) in slow stream of commercial O or N; (4) in H at different pressures.

Conclusions were as follows: Pt and Rh disintegration about five times as great in O as in air; in air at 25 mm about one-half that at 760 mm; and in N disintegration

is very small. Ir disintegration in air about ten times as great as Pt. At 25 mm Ir loss in weight equals one-eighth that at 760 mm, while in O it is about eleven times as great as in air.

"On the condensation nuclei produced in air and hydrogen by heating a platinum wire," by Gwilym Owen, *Phil. Mag.*, 6, p. 306; 1903.

Condensation nuclei from heated Pt wire were produced in an atmosphere of air at 300° C. The size and number of nuclei are increased with increased temperature. In the case of hydrogen the results are obtained at temperatures some 600° or 700° higher than in air; in fact, not until the wire is luminous.

Platinum laboratory utensils, by Percy H. Walker and F. W. Smithers, *Bu. of Chem.*, Bull. No. 137, p. 180, November, 1910.

Apparently the pioneer paper demonstrating the desirability of determining the quality of platinum ware purchased for exact analytical purposes.

Preliminary report of the committee on "Quality of platinum laboratory utensils," by W. F. Hillebrand, Percy H. Walker, and E. T. Allen, *J. Indus. & Eng. Chem.*, 8, No. 9, September, 1911.

Report of progress by committee on "Quality of platinum laboratory utensils," April 9, 1914, *J. Indus. & Eng. Chem.*, June, 1914.

"The vapor pressure of the metals platinum and molybdenum," by Irving Langmuir and G. M. J. Mackay, *Phys. Rev.*, IV, No. 4, p. 377, October, 1914.

The method consists in determining the loss of weight undergone by wires of the two metals maintained electrically at various temperatures for definite periods of time in glass vessels exhausted to an exceptionally good vacuum.

The calculation of the vapor pressure from the rate of loss of weight at a definite temperature is based upon the kinetic theory of gases and the Clausius-Clapeyron formula giving the relation between the vapor pressure of any substance and the temperature.

The rate of evaporation of heated platinum and molybdenum wires in high vacuum were determined over wide ranges of temperature. From these data the vapor pressures of these metals were calculated. The evaporation per square centimeter per second was determined and also the latent heat of vaporization in calories per gram atom.

"Chemical reactions at low pressures," by Dr. Irving Langmuir, *J. Indus. & Eng. Chem.*, 7, p. 349, 1915; *J. Am. Chem. Soc.*, 37, p. 1139, 1915.

Dr. Langmuir advances the "theory of molecular films" to explain heterogeneous reactions occurring between heated filaments and the surrounding gases. The adsorption film is taken to be in a state of kinetic equilibrium with the gases around it, and is in a state of constant change. The majority of gas molecules striking the bare surface of the film are held by cohesive forces until they evaporate. The rate of formation of the adsorption film is proportional to the gas pressure and to the area of the uncovered surface. The reactions observed may be divided into four classes:

1. The filament is attacked by the gas.
2. The gas reacts with vapor given off by the filament.
3. The filament acts catalytically on the gas, producing a chemical change in the gas without any permanent change in the filament.

4. The gas is chemically changed or reacts with the filament as a result of electrical discharge through the gas.

The application of this theory to particular cases was considered and included platinum reactions under classes 2 and 3.

"The sublimation of metals at low pressures," by G. W. C. Kaye, B. A., D. Sc., and Donald Ewen, M. Sc., *Pro. Roy. Soc., Lon.*, 89-A, p. 58, 1913-14.

The "Rectilinear emission of particles," from the surface of electrically heated strips of Ir, Cu, Fe, W, is discussed. There appear to be two main classes of vapor given out when a metal volatilizes, one kind, which is associated with evaporation as usually understood by the term, the other, made up of particles of metal, which travel in straight lines from the surface of the metal. It is suggested that the difference between the two classes is that the latter are charged electrically, while the former are electrically neutral. A deposit taking the outline of the heated strip or the shape of an interposed screen could be obtained readily in the case of the above metals heated to about 1000° C in nitrogen at about 20 mm pressure.

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WASHINGTON, March 28, 1915.

